

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
10 May 2002 (10.05.2002)

PCT

(10) International Publication Number
WO 02/36727 A1

- (51) International Patent Classification: **C11D 3/386** 3-1-5 Koyo-chonaka, Higashinada-ku, Kobe 658-0032 (JP). OHTANI, Ryohei [JP/JP]; 7-19, Ueda Naka-machi, Nishinomiya 663-8134 (JP).
- (21) International Application Number: PCT/US00/00925
- (22) International Filing Date: 14 January 2000 (14.01.2000) (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).
- (25) Filing Language: English
- (26) Publication Language: English (81) Designated State (national): JP.
- (71) Applicant: THE PROCTER & GAMBLE COMPANY Published:
[US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). — with international search report
- (71) Applicants and
- (72) Inventors: KHAN, Golam, Faruque [BD/JP]; #1-1703, For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/36727 A1

(54) Title: A DETERGENT COMPOSITION COMPRISING A METALLO PROTEASE AND CALCIUM ION

(57) Abstract: A detergent composition of the present invention contains a deterative surfactant, a metallo protease and a calcium ion.

A DETERGENT COMPOSITION COMPRISING
A METALLO PROTEASE AND CALCIUM ION

5

10

FIELD OF THE INVENTION

The present invention relates to detergent compositions that comprise a protease. More particularly, the present invention relates to laundry detergent compositions, dishwashing detergent compositions, hard surface cleaning compositions and personal cleansing compositions that comprise a metallo-protease.

BACKGROUND OF THE INVENTION

20

Various types of enzymes have long been used in laundry detergents to assist in the removal of certain stains from fabrics. Each class of enzyme (amylases, proteases, lipases, cellulases, etc.) generally catalyzes a different chemical reaction. For example, protease enzymes are known for their activity to hydrolyze (break down a compound into two or more simpler compounds) other proteins. Many food products and other organic materials contain proteins that stain fabric materials, such as clothing. Protease enzymes can help remove these stains by breaking down the proteins. Naturally occurring or engineered protease enzymes have been added to laundry detergent compositions for this reason.

30

Protease enzymes are divided into four groups, serine protease, cysteine protease, aspartic acid protease and metallo protease. Although the use of

serine protease has been investigated for use in detergent compositions for several years, metallo protease has not been used in detergent compositions for many reasons. For example, the stability and the activity of metallo protease in a detergent solution, the effect of chelating agents on the metallo protease, the effect of metallo protease on various fabric materials were all unknown. Thus, there were too many unknown parameters to ensure satisfactory stability.

However, there is a continuing need for proteases that provide improved stability when used in detergent and cleaning compositions during the storage.

It has now been found that a detergent composition containing a metallo protease and a calcium ion is effective for removing soils, and is stable during the storage.

SUMMARY OF THE INVENTION

The present invention relates to detergent compositions comprising: a deterative surfactant; a metallo protease; and a calcium ion. The metallo-protease of the present invention has more than 15AU/mg of caseinolytic activity.

The present invention can provide an improved protease storage stability in detergent composition.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

25

While the specification concludes with claims particularly pointing out and distinctly claiming the invention, it is believed the present invention will be better understood from the following description.

Definitions

All percentages are by weight of total composition unless specifically stated otherwise.

5 All ratios are weight ratios unless specifically stated otherwise.

As used herein, "comprising," means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties.

10 Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

As used herein, the term "detergent composition" or "detergent" is intended to designate any of the agents conventionally used for removing soil, such as general household detergents or laundry detergents of the synthetic or
15 soap type.

The detergent composition of the present invention

The detergent composition of the present invention contains a metallo protease and a calcium ion. The detergent composition preferably contain from
20 about 0.0001% to about 5%, preferably from about 0.001% to about 0.25% by weight of a metallo protease and from about 1 to 200 micromole, preferably from about 5 to about 50 micromole per liter of a calcium ion.

Particularly, the detergent composition of the present invention contains from about 0.01% to 60% by weight of a deterative surfactant, from about 0% to
25 80% by weight of a detergent builder, from about 0.0001% to about 5% by weight of a metallo protease, and from about 1 to about 200 millimoles per liter of calcium ions.

Metallo protease

30 Metallo protease is an essential ingredient of the present invention. The metallo protease in the detergent composition of the present invention has more

than 15 AU/mg of caseolytic activity by the Caseolytic-test method described in detail below. Any metallo proteases can be used as long as it has more than 15 AU/mg of caseolytic activity.

The metallo-protease in the detergent compositions of the present invention optionally have these characteristics: a) a molecular weight from about 28KDa to about 40KDa, preferably, from about 30 KDa to about 36 KDa; and (b) Zn, Co, Mn or Cu as an active center, preferably, Zn (Zinc) as an active center. The metallo protease having a zinc active center are called zinc metallo protease.

The metallo-protease in the detergent compositions of the present invention can be derived from a natural resource or recombinant. If the metallo-protease is derived from a natural resource, the natural resource is bacterium preferably *Bacillus subtilis*, see D. Tsuru & T. Yoshimoto, 'Microbial Proteases', Handbook of Microbiology, 2nd Edition by A.I. Laskin & H.A. Lechevalier, 239-283. The metallo-protease can also be derived from commercially available products such as Protease NTM by Amano Seiyaku Co., Ltd (Tokyo, Japan), as Orientase 90NTM of Hankyu Bio-industries Corp. Ltd (Osaka, Japan). Examples of preferable metallo proteases are disclosed in PCT/US99/07245.

Some commercially available protease products contain both metallo protease and serine protease. If using these commercially available products to derive the metallo protease of the present invention, it is preferable to purify these commercial products. One preferable purification method is disclosed in PCT/US99/07246 filed on April 1, 1999

One example how to obtain a metallo protease from commercial available protease products is as follows:

(a) prepare 400 ml of crude samples using Protease NTM (provided by Amano Seiyaku, Japan, Tokyo), in 25 mM sodium phosphate buffer of pH 6 at 25°C. The concentration is adjusted to 10 mg/ml.

(b) concentrate the solution from step (a) by Pellicon concentrator (Millipore) with Pellicon XL filter (Molecular Weight cut of 5k) and obtained a 40 ml concentrated solution.

(c) add 360 ml of 25 mM sodium phosphate buffer of pH 6 to the solution from step (b) to obtain 400 ml of solution. Repeat steps (b) and (c) twice with this solution, to obtain about 40 ml of solution.

(d) add about 360 ml of Milli-Q water to the solution from step (c) and obtain 400 ml of a solution and adjust the pH to 6.7 with a few drops of 0.1M NaOH.

This solution can be further concentrated by Pellicon concentrator to 80 - 100 ml.

(e) Incubate the solution from step (d) for 24 hours at 4°C in the refrigerator (Mitsubishi) to obtain a white precipitate.

(f) Centrifuge the mixer from step (e) in a centrifuge, for example, CR 5B, Hitachi, at 4000 rpm for 15 minutes. Wash the precipitate twice with Milli-Q water. Then freeze dry the precipitate to obtain about 1g of precipitate.

The precipitate should contain about 30% of active metallo-protease with 58 AU/mg of caseinolytic activity.

Metallo proteases can be distinguished from traditional serine proteases from the following points: Metal proteases have a metal active center as described above, but serine proteases do not. Metallo proteases have an optimum pH in the range of from about 6.5 to 7.5, serine proteases have an optimum pH above 8.0.

Caseinolytic-test

The Caseinolytic-test is used for measuring the hydrolysis rate of a metallo protease. This method uses casein as a protein substrate and measures the rate of hydrolysis of casein (dimethyl casein, DMC) by the metallo protease. The detailed method is as follows:

5.5mg/ml of DMC (Sigma) is prepared in 0.1 M tris-HCl buffer of pH 7.0 and 0.1 ml of metallo protease solution is mixed with 0.9 ml of the casein solution, and the hydrolysis is carried out at 20 °C. After 10 minutes, 4 ml of TCA solution (0.11 M $\text{C Cl}_3\text{COOH}$ + 0.22 M $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ + 0.33 M CH_3COOH) is added to the metallo protease-casein mixture and incubated 30 minutes at 20

°C. Then, the white mixture is centrifuged at 12000 rpm for 8-10 minutes. 5 ml of the supernatant is transferred to a disposable cuvette and 2.5 ml of 0.5 M Na₂CO₃ was added. After 5-10 minutes, 0.5ml of phenol reagent (1ml Folin Ciocalteu's phenol reagent, Sigma, with 5ml milli-Q water) is added and incubated at room temperature for 40 minutes. Then, absorbance at 660 nm is measured against water. One Anson unit (AU) of metallo protease activity is defined as the amount of enzyme that increases the absorbance corresponding to 1 micromole of tyrosine in 1 minute under the above mentioned measuring conditions. According to this test, the metallo protease in the detergent composition has more than 15 AU/mg, preferably, more than 30 AU/mg.

The detergent composition of the present invention comprises, preferably, from about 0.0001% to about 5%, more preferably from about 0.001% to about 0.2%, even more preferably from about 0.005% to about 0.1% by weight of the metallo protease.

Calcium ion

Calcium ion is also an essential ingredient of the present invention. Not wanting to be limited by theory, metallo proteases usually have three or four binding sites for calcium ions in the molecule. When a calcium ion binds to active site, metallo proteases may change their three dimensional structure to a more stable configuration. As a result, metallo proteases can retain their activity during storage.

However, chelating agents are often used in detergent compositions. These chelating agents may gradually bind with the calcium ions associated with the metallo protease during storage. This causes the metallo proteases to lose calcium ions in the molecule, and then become inactive. Thus, sufficient calcium ions are necessary in the detergent composition to allow for the scavenging by the chelating agents.

Calcium ion can be added in salt form. Any calcium salts can be used for adding calcium ions. Preferable calcium salts are selected from the group consisting of calcium sulfate, calcium phosphate, calcium chloride, calcium

acetate, calcium citrate and mixtures thereof. Calcium ion can be added to the detergent composition of the present invention in the range of from about 1 to about 200 millimoles per liter, preferably, from about 2 to about 100, more preferable, from about 5 to about 50 millimoles per liter.

5

Detersive surfactant

The detergent compositions of the present invention include a surfactant that can be selected from the group consisting of nonionic, anionic, cationic, ampholytic, zwitterionic, semi-polar surfactants, and mixtures thereof.

10

The surfactant is typically present at a level of from about 0.01% to about 60% by weight. More preferred levels of incorporation are from about 1% to about 35% by weight, most preferably from about 1% to about 30% by weight of detergent compositions in accord with the invention.

15

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

20

Preferred surfactants to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

25

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol.

30

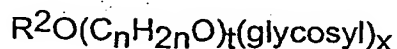
Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-

102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactants of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohol having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful nonionic surfactants of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

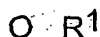
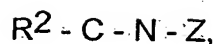
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic deterative surfactant of the present

invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

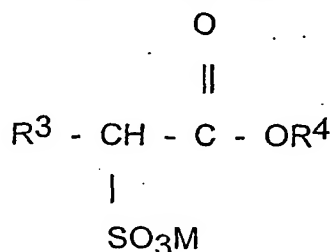


5

wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R^1 is methyl, R^2 is a
10 straight C_{11-15} alkyl or C_{16-18} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfate, branched alkyl sulfate, methyl-branched alkyl sulfate
15 surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

20 The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



25

wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable

salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10} - C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates
5 wherein R^3 is C_{10} - C_{16} alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10} - C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10} - C_{20} alkyl component, more preferably a C_{12} - C_{18} alkyl or hydroxyalkyl, and M is H or
10 a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and
15 mixtures thereof, and the like). Typically, alkyl chains of C_{12} - C_{16} are preferred for lower wash temperatures (e.g. below about 50°C) and C_{16} - C_{18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for deterative purposes can also be included in the detergent compositions of the present invention. These can
20 include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8 - C_{22} primary or secondary alkanesulfonates, C_8 - C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification
25 No. 1,082,179, C_8 - C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates

(especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below),
5 branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_k-CH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

10 Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

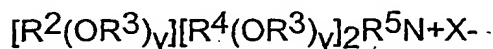
15 When included therein, the detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)_mSO₃M
20 wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for
25 example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and
30 dimethyl piperdinium cations and those derived from alkylamines such as

ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate (C₁₂-C₁₈E(1.0)M), C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate (C₁₂-C₁₈E(2.25)M), C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate (C₁₂-C₁₈E(3.0)M), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₈E(4.0)M), wherein M is conveniently selected from sodium and potassium.

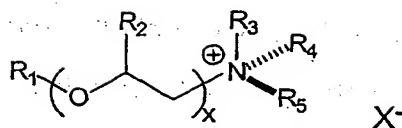
The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



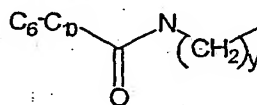
wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain; each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the
 5 formula (II) :



Formula II

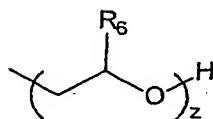
y is 2-4, preferably 3.

10 whereby R2 is H or a C1-C3 alkyl,

whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short
 chain alkyl (C1-C3) or alkoxyated alkyl of the formula III,

15 whereby X- is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

R6 is C1-C4 and z is 1 or 2.

20 Preferred quaternary ammonium surfactants are those as defined in
 formula I whereby

R1 is C8, C10 or mixtures thereof, x=0,

R3, R4 = CH3 and R5 = CH2CH2OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



- 5 wherein R_1 is C_8 - C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl.

The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is
10 derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- 15 coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
20 coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
choline esters (compounds of formula (i) wherein R_1 is
25 $CH_2-CH_2-O-C-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).



di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

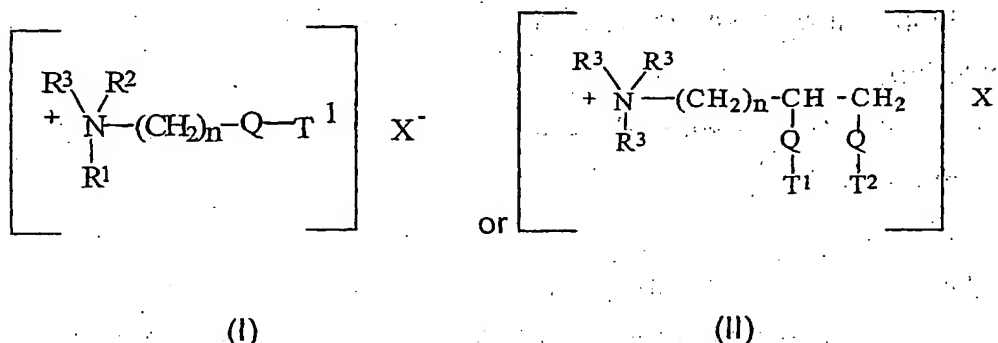
Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives or their corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C₁₂₋₁₄ alkyl hydroxyethyl dimethylammonium chloride;
- 11) C₁₂₋₁₈ alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallow-oxy-ethyl) dimethylammonium chloride;
- 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, -NR⁴-C(O)-, -C(O)-NR⁴-;

10 R¹ is (CH₂)_n-Q-T² or T³;

R² is (CH₂)_m-Q-T⁴ or T⁵ or R³;

R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;

R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;

T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;

15 n and m are integers from 1 to 4; and

X⁻ is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or
20 branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

25 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;

- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 10 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride; and
- 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride; and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

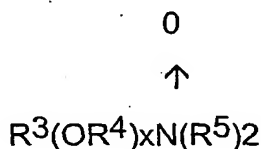
Zwitterionic surfactants are also suitable for use in detergent compositions. These surfactants can be broadly described as derivatives of

secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for
 5 examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic
 10 surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from
 15 the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

20 Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



25 wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide
 30 group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups

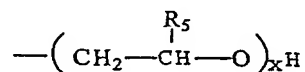
can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

- 5 When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

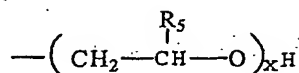
The detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

- 10 Suitable primary amines for use herein include amines according to the formula R₁NH₂ wherein R₁ is a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain or R₄X(CH₂)_n, X is -O-, -C(O)NH- or -NH-, R₄ is a C₆-C₁₂ alkyl chain n is between 1 to 5, preferably 3. R₁ alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.
- 15 Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C₈-C₁₀ oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.
- 20 Suitable tertiary amines for use herein include tertiary amines having the formula R₁R₂R₃N wherein R₁ and R₂ are C₁-C₈ alkylchains or



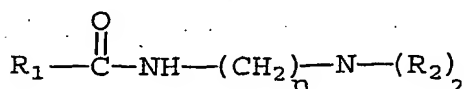
- R₃ is either a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain, or R₃ is R₄X(CH₂)_n, whereby X is -O-, -C(O)NH- or -NH-, R₄ is a C₄-C₁₂, n is between 1 to 5, preferably 2-3. R₅ is H or C₁-C₂ alkyl and x is between 1 to 6.
- 25 R₃ and R₄ may be linear or branched ; R₃ alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are $R_1R_2R_3N$ where R_1 is a C6-C12 alkyl chain, R_2 and R_3 are C1-C3 alkyl or



5 where R_5 is H or CH3 and $x = 1-2$.

Also preferred are the amidoamines of the formula:



wherein R_1 is C6-C12 alkyl; n is 2-4,

10 preferably n is 3; R_2 and R_3 is C1-C4

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

ADDITIONAL INGREDIENTS

25 Builder

The compositions according to the present invention may further comprise a builder. Any conventional builder is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic

acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid.

5 Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6
10 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy
15 groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623.
20 Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates
25 described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate
30 derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British

Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-
5 tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis -
dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -
hexacarboxylates and and carboxymethyl derivatives of polyhydric alcohols
such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic
acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent
10 No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builders for use in the present compositions include a mixture of
a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate
15 (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.
Other preferred builders include a mixture of a water-insoluble aluminosilicate
builder such as zeolite A, and a watersoluble carboxylate chelating agent such as
citric acid. Preferred builders for use in liquid detergent compositions of the
present invention are soaps and polycarboxylates.

20 Other builder materials that can form part of the builder for use in granular
compositions include inorganic materials such as alkali metal carbonates such as
citrate, bicarbonates, silicates, and organic materials such as the organic
phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

Other suitable water-soluble organic salts are the homo- or co-polymeric
25 acids or their salts, in which the polycarboxylic acid comprises at least two
carboxyl radicals separated from each other by not more than two carbon atoms.
Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts
are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride,
such copolymers having a molecular weight of from 20,000 to 70,000, especially
30 about 40,000.

Detergency builder salts are normally included in amounts of from 0% to about 80% by weight of the composition preferably from about 5% to 80%, more preferably, from about 10% to about 70% and most usually from about 30% to about 60% by weight.

detergent enzymes

The detergent compositions can further comprise one or more enzymes in addition to the metallo proteases described above, which provide cleaning performance, fabric care and/or sanitisation benefits.

These additional enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, serine-proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase and mixtures thereof.

A preferred combination is a detergent composition having cocktail of conventional applicable enzymes like serine-protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800.

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxasine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-

methoxyphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R (Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable serine-proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable serine-protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred serine-protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156,

+166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

Also suitable for the present invention are serine-protease described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH serine-protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising serine-protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a serine-protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable serine-proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes detergent compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in detergent compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be

mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special attention must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO

9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora
5 et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation s are also described, for
10 example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Color care and fabric care benefits

Technologies which provide a type of color care benefit can also be included. Examples of these technologies are metallo catalysts for color
5 maintenance. Such metallo catalysts are described in copending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer for color care treatment and perfume substantivity are further examples of color care / fabric care technologies and are described in the co-pending
10 Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic
15 fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening s include high molecular weight
20 polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide
25 materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some
30 instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Bleaching agent

Additional optional detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents.

5 Preferred peroxygen bleaching agents include those peroxygen bleaching compounds which are capable of yielding hydrogen peroxide in an aqueous solution. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the
10 alkali metal perborates, percarbonates, perphosphates, and the like.

Preferred peroxygen bleaching agents include peroxygen bleach selected from the group consisting of perborates, percarbonates, peroxyhydrates, peroxides, persulfates, and mixtures thereof. Specific preferred examples include: sodium perborate, commercially available in the form of mono- and
15 tetra-hydrates, sodium carbonate peroxyhydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Particular preferred are sodium perborate tetrahydrate, and especially, sodium perborate monohydrate. Sodium perborate monohydrate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching
20 solution.

These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

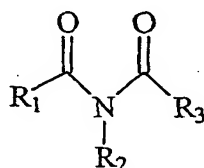
25 The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses
30 percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the

magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxypropionic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetythylenediamine (TAED), nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5-trimethylhexanoyloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7 and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



wherein R₁ is a C₇-C₁₃ linear or branched chain saturated or unsaturated alkyl group, R₂ is a C₁-C₈, linear or branched chain saturated or unsaturated alkyl

group and R₃ is a C₁-C₄ linear or branched chain saturated or unsaturated alkyl group.

Useful bleaching agents, including peroxyacids and bleaching s comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-
5 pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen
10 peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic s are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and
15 manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

20 Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with
25 light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated
30 zinc phthalocyanine.

Chelating Agents

The detergent compositions herein may also optionally contain one or
5 more iron and/or manganese chelating agents. Such chelating agents can be
selected from the group consisting of amino carboxylates, amino phosphonates,
polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as
hereinafter defined. Without intending to be bound by theory, it is believed that
10 the benefit of these materials is due in part to their exceptional ability to remove
iron and manganese ions from washing solutions by formation of soluble
chelates.

Amino carboxylates useful as optional chelating agents include
ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilo-
triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates,
15 diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium,
and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the
compositions of the invention when at least low levels of total phosphorus are
permitted in detergent compositions, and include ethylenediaminetetrakis
20 (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates
to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in
the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to
Connor et al. Preferred compounds of this type in acid form are
25 dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine
disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent
4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine
30 diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with,
for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

5

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^R.

30

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

5 Others

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, tarnish inhibitors, coloring agents, and/or encapsulated
10 or non-encapsulated perfumes.

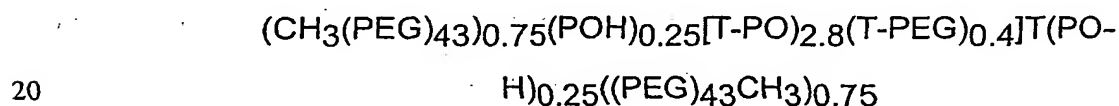
Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from ungelatinized starch acid-esters of substituted
15 dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified
20 by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-
25 stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4" -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium
30 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6- ylamino)stilbene-2,2'disulphonate, sodium 2(stilbyl-4"-(naphtho-1',2':4,5)-1,2,3 - triazole-2"-

sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1,2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3,000. The polyesters and their method of preparation are described in detail in EPA 311 342.

The enzyme stabilizer useful herein depends upon characteristics such as the enzyme used, and the active ingredient. However, preferred examples of an enzyme stabilizer useful herein includes calcium ion, borates, borate-diols, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof.

It is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxyated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxyated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

5 In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions.

EXAMPLES

10 The following examples further describe and demonstrate the preferred embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration, and are not to be constructed as limitations of the present invention since many variations thereof are possible without departing from its spirit and scope.

Examples 1

Liquid Hard Surface Cleaning Compositions

		Example No.						
Component		A	B	C	D	E	F	G
5	Metallo-protease	0.001	0.005	0.01	0.02	0.03	0.01	0.02
	Serine-Protease	-	-	-	-	-	0.02	0.01
	EDA*	-	-	-	2.90	2.90	-	-
	C ₁₃ linear alky	-	1.95	-	1.95	-	1.95	-
	benzene sulfonate							
10	(LAS)							
	Alkyl sulfate (AS)	2.00	-	2.20	-	2.20	-	2.20
	Alkylpolyoxyethylene sulfate (AES)	2.00	-	2.20	-	2.20	-	2.20
	Amine Oxide	0.40	-	0.50	-	0.50	-	0.50
15	Hydrotrope	-	1.30	-	1.30	-	1.30	-
	Solvent**	-	6.30	6.30	6.30	6.30	6.30	6.30
	CaCl ₂ ***	10.0	20.0	30.0	-	-	-	-
	CaSO ₄	-	-	-	10.0	-	-	-
20	Ca ₃ (PO ₄) ₂	-	-	-	-	10.0	-	-
	Calcium acetate	-	-	-	-	-	10.0	-
	Calcium citrate	-	-	-	-	-	-	10.0
25	<u>Water and Minors</u>	<u>balance to 100%</u>						

*Na₄ ethylenediamine diacetic acid

**Diethyleneglycol monohexyl ether

***All values of calcium salts are described as millimole.

Examples 2

Dishwashing Composition

		Example No.					
Component		A	B	C	D	E	F
5	Metallo-protease	0.001	0.005	0.01	0.05	0.01	0.03
	Serine-protease	-	-	-	-	0.04	0.01
	TFAA*	0.90	0.90	0.90	0.90	0.90	0.90
	AES	12.00	12.00	12.00	12.00	12.00	12.00
	2-methyl undecanoic acid	4.50	4.50	-	4.50	4.50	-
10	C ₁₂ alcohol ethoxylate (4)	3.00	3.00	3.00	3.00	3.00	3.00
	Amine oxide	3.00	3.00	3.00	3.00	3.00	3.00
	Hydrotrope	2.00	2.00	2.00	2.00	2.00	2.00
	Ethanol	4.00	4.00	4.00	4.00	4.00	4.00
	MgCl ₂	0.20	0.20	0.20	0.20	0.20	0.20
15	CaCl ₂ **	5.0	15.0	20.0	25.0	30.0	35.0
<u>Water and Minors</u>		<u>balance to 100%</u>					

*C₁₆-C₁₈ alkyl N-methyl glucamide

**All values of calcium salts are described as millimole.

Example 3

Granular Fabric Cleaning Composition

5	Component	Example No.			
		A	B	C	D
	Metallo-protease	0.01	0.02	0.02	0.02
	Serine-protease	-	-	0.01	0.02
	C ₁₃ linear alkyl benzene sulfonate	22.00	22.00	22.00	22.00
	Phosphate (as sodium	23.00	23.00	23.00	23.00
10	tripolyphosphates)				
	Sodium carbonate	23.00	23.00	23.00	23.00
	Sodium silicate	14.00	14.00	14.00	14.00
	Zeolite	8.20	8.20	8.20	8.20
	DPTA*	0.40	-	0.40	-
15	CaCl ₂ ***	10.0	-	-	-
	CaSO ₄	-	-	10.0	-
	Ca ₃ (PO ₄) ₂	-	-	10.0	-
20	Calcium acetate	-	-	-	10.0
	Sodium sulfate	5.50	5.50	5.50	5.50
	Water	balance to 100%			

*Diethylene triamine pentaacetic acid

**All values of calcium salts are described as millimole.

Example 4

Liquid Fabric Cleaning Compositions

		<u>Example No.</u>	
<u>Component</u>		<u>A</u>	<u>B</u>
5	DI H ₂ O	38.63	-
	MEA (monoethanolamine)	0.48	9.00
	NaOH	4.40	1.00
	Pdiol	4.00	10.0
	Citric acid	2.50	2.00
10	Sodium sulfate	1.75	-
	DTPA	0.50	1.00
	FWA Premix (Br 15/MEA/NI 23-9)	0.15	0.15
	Na C25AE1.80S	23.50	-
	AE3S (H)	-	4.00
15	C11.8HLAS*	3.00	14.00
	Neodol	2.00	6.00
	EtOH	0.50	2.00
	CaCl ₂ ***	15.00	30.00
	Borax premix (Borax/MEA/Pdiol/Citric Acid)	2.50	-
20	Boric acid	-	1.00
	C10 amido propyl dimethyl amine	1.50	-
	TEPA 105**	1.20	-
	Dye	0.0040	0.0015
	Cellulase	0.053	0.20
25	Amylase	0.15	0.20
	Metallo-protease	0.05	0.05
<u>Waters and minors</u>		<u>up to 100%</u>	

*HLAS : Acid form of linear alkyl benzene sulfonate (a synthetic anionic surfactant)

30 **TEPA :tetraethylene pentamine

***All values of calcium salts are described as millimole.

The compositions of the present invention can be suitably prepared by any process chosen by the formulator, non-limiting examples of which are described in U.S. 5,691,297 Nassano et al., issued November 11, 1997; U.S. 5,574,005 Welch et al., issued November 12, 1996; U.S. 5,569,645 Dinniwell et al., issued October 29, 1996; U.S. 5,565,422 Del Greco et al., issued October 15, 1996; U.S. 5,516,448 Capeci et al., issued May 14, 1996; U.S. 5,489,392 Capeci et al., issued February 6, 1996; U.S. 5,486,303 Capeci et al., issued January 23, 1996 all of which are incorporated herein by reference.

In addition to the above examples, the cleaning compositions of the present invention can be formulated into any suitable laundry detergent composition, non-limiting examples of which are described in U.S. 5,679,630 Baeck et al., issued October 21, 1997; U.S. 5,565,145 Watson et al., issued October 15, 1996; U.S. 5,478,489 Fredj et al., issued December 26, 1995; U.S. 5,470,507 Fredj et al., issued November 28, 1995; U.S. 5,466,802 Panandiker et al., issued November 14, 1995; U.S. 5,460,752 Fredj et al., issued October 24, 1995; U.S. 5,458,810 Fredj et al., issued October 17, 1995; U.S. 5,458,809 Fredj et al., issued October 17, 1995; U.S. 5,288,431 Huber et al., issued February 22, 1994 all of which are incorporated herein by reference.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from the scope of the present invention.

WHAT IS CLAIMED IS:

1. A detergent composition comprising:

- (a) a deterative surfactant;
- (b) a metallo protease; and
- (c) a calcium ion,

5 wherein the metallo-protease has at least more than 15AU/mg of caseinolytic activity

2. The detergent composition according to Claim 1, wherein the detergent composition comprises from about 0.0001% to about 5% by weight of the metallo-protease

3. The detergent composition according to Claim 2, wherein the deterative surfactant is selected from the group consisting of anionic surfactants, nonionic surfactants, zwitterionic surfactants, ampholytic surfactants, cationic surfactants, and mixtures thereof.

5

4. The detergent composition according to Claim 1, wherein the detergent composition comprises from about 1 to about 200 millimoles per liter of calcium ions.

5. The detergent composition according to Claim 1, wherein the metallo protease has a metal active center selected from the group consisting of Zn, Co, Mn or Cu.

6. The detergent composition according to Claim 1, wherein the calcium ion is added as a salt selected from the group consisting of calcium sulfate, calcium phosphate, calcium chloride, calcium acetate, calcium citrate and mixtures thereof.

5

7. A detergent composition comprising:

- (a) from about 0.01% to 60% by weight of a deterative surfactant;
- (b) from about 0% to 80% by weight of a detergent builder;
- (c) from about 0.0001% to about 5% by weight of a metallo protease; and
- (d) from about 1 to about 200 milimoles per liter of calcium ions.

8. The detergent composition according to Claim 7, the deterative surfactant is selected from the group consisting of anionic surfactants, nonionic surfactants, zwitterionic surfactants, ampholytic surfactants, cationic surfactants, and mixtures thereof and the detergent builder is selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher phosphates, alkali metal carbonates and bicarbonates, alkali silicates, aluminosilicates, polycarboxylates, citrates and mixtures thereof.

9. The detergent composition according to Claim 7, further comprising a bleach.

10. The detergent composition according to Claim 9, wherein the bleach is selected from the group consisting of perborates, percarbonates, peroxyhydrates, peroxides, persulfates, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

PCT/US 00/00925

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 590 746 A (GRACE W R & CO) 6 April 1994 (1994-04-06) claims; examples 8,11,15	1-9
X	US 3 764 542 A (NATALI R ET AL) 9 October 1973 (1973-10-09) column 3 -column 4	1
A	WO 99 14342 A (GENENCOR INTERNATIONAL B V)) 25 March 1999 (1999-03-25) page 17 -page 18; claims	1
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

14 September 2000

Date of mailing of the international search report

25/09/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Pfannenstein, H

INTERNATIONAL SEARCH REPORT

ternation ication No

PCT/US 00/00925

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 199326 Derwent Publications Ltd., London, GB; Class D13, AN 1993-211300 XP002147325 & JP 05 137573 A (TOSOH CORP), 1 June 1993 (1993-06-01) abstract	1
A	US 4 305 837 A (KAMINSKY GEORGE J ET AL) 15 December 1981 (1981-12-15) claims	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

ation No

PCT/US 00/00925

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0590746	A	06-04-1994	AT 162499 T	15-02-1998
			CA 2106609 A	29-03-1994
			DE 69316501 D	26-02-1998
			DE 69316501 T	10-09-1998
			ES 2111710 T	16-03-1998
			JP 6262165 A	20-09-1994
US 3764542	A	09-10-1973	NONE	
WO 9914342	A	25-03-1999	AU 9312398 A	05-04-1999
			EP 0958368 A	24-11-1999
JP 5137573	A	01-06-1993	NONE	
US 4305837	A	15-12-1981	CA 1153964 A	20-09-1983
			MX 151009 A	06-09-1984
			PH 15652 A	11-03-1983

THIS PAGE BLANK (USPTO)